DENVER FRONT RANGE STUDY
DIOXINS IN SURFACE SOIL

Study 2: Characterization of Dioxins, Furans and PCBs In Random Soil Samples Collected from The Rocky Mountain Arsenal

July 2001

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LIST OF ACRONYMS AND ABBREVIATIONS

Ah	aryl hydrocarbon
ATSDR	Agency for Toxic and Disease Registry
CAS	Columbia Analytical Services
COC	Contaminant of Concern
D/F	dioxin/furan
EMPC	Estimated Maximum Potential Concentration
HRGC/MS	High Resolution Gas Chromatography/Mass Spectrometry
LCS	Laboratory Control Sample
MDL	Method Detection Limit
MQL	Method Quantitation Limit
MRI	Midwest Research Institute
NPL	National Priority List
OCP	organochlorine pesticide
PARCC	Precision, Accuracy, Representativeness, Comparability, and Completeness
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzodioxin
PCDF	polychlorinated dibenzofuran
PE	Performance Evaluation
ppt	parts per trillion (1 microgram per kilogram)
QA/QC	Quality Assurance/Quality Control
QATS	Quality Assurance Technical Support
RMA	Rocky Mountain Arsenal
SOP	Standard Operating Procedure
TCDD	2,3,7,8-tetrachlorodibenzo-*p*-dioxin
TEF	Toxicity Equivalency Factor
TEQ	2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) equivalents
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

LIST OF CHEMICAL ABBREVIATIONS

HpCB	heptachlorobiphenyl
HpCDD	heptachlorodibenzodioxin
HpCDF	heptachlorodibenzofuran
HxCB	hexachlorobiphenyl
HxCDD	hexachlorodibenzodioxin
HxCDF	hexachlorodibenzofuran
OCDD	octachlorodibenzodioxin
OCDF	octachlorodibenzofuran
PeCB	pentachlorobiphenyl
PeCDD	pentachlorodibenzodioxin
PeCDF	pentachlorodibenzofuran
TCB	tetrachlorobiphenyl
TCDD	*2,3,7,8*-tetrachlorodibenzo-*p*-dioxin
TCDF	tetrachlorodibenzofuran

1.0 INTRODUCTION

1.1 Site Description

The Rocky Mountain Arsenal (RMA) is a parcel of approximately 27 square miles of land located north-east of Denver, Colorado. The RMA was previously used by the US Army for manufacturing and testing of munitions, and was subsequently used by Shell Oil Company for the manufacture of pesticides. Because of extensive chemical contamination in the central portion of the site, the United States Environmental Protection Agency (USEPA) became involved in studies to clean up RMA in 1982, and the site was placed on National Priorities List (NPL) in 1987. The chemicals of principal health concern at RMA vary from location to location, and include pesticides, metals, solvents, chemical process intermediates, and chemical warfare agents. In particular, several organochlorine pesticides (OCPs), mainly aldrin and dieldrin, are major contaminants of concern (COCs), as well as a number of their intermediates and degradation products (USEPA 1999).

Some members of the public stated they were concerned that RMA might be contaminated with dioxins. A review of this question was performed by Gannett Fleming (1999), and USEPA Region 8 concluded that data available at the time were insufficient to determine whether dioxins should or should not be considered chemicals of potential concern at RMA. In order to investigate this question, USEPA Region 8, working in cooperation with the State of Colorado and the Rocky Mountain Arsenal Remedial Venture Office, has undertaken a series of studies to characterize the levels of dioxins in on-site and off-site soils. This purpose of this study is to summarize data on the levels of dioxin in random soil samples collected from across RMA, and to compare the site data with the regional ambient data in order to judge whether levels at RMA are elevated compared to other comparable locations in and about the greater Denver area, and, if so, whether the levels are in a range of potential human health concern to on-site workers.

Other reports which are part of this project and which provide additional information on the absolute and relative level of dioxins in on-site and off-site soils include:

Denver Front Range Study. Dioxins in Surface Soil. Study 3: Western Tier Parcel, Rocky Mountain Arsenal (USEPA 2001a)

Denver Front Range Study. Dioxins in Surface Soil. Study 4: Characterization of Dioxins, Furans and PCBs In Soil Samples Collected from Historic Use Areas the Rocky Mountain Arsenal (USEPA 2001b)

Denver Front Range Study. Dioxins in Surface Soil. Study 1: Characterization of Dioxins, Furans and PCBs In Soil Samples Collected from the Denver Front Range Area (USEPA 2001c)

1.2 Definition of Dioxins

"Dioxin" is usually used as a synonym for *2,3,7,8*-tetrachlorodibenzo-*p*-dioxin (TCDD). The toxicity of TCDD is believed to be initiated by binding of the TCDD molecule to a cellular protein referred to as the aryl-hydrocarbon (Ah) receptor. However, there are many different chemicals besides TCDD that can bind to this receptor and trigger some or all of the toxic responses that are associated with TCDD exposure. This includes some other members (congeners) of the polychlorinated dibenzodioxin (PCDD) class, as well as some polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), other types of halogenated (e.g., brominated) dioxins and furans, as well as various other chlorinated hydrocarbons (e.g. chlorinated naphthalenes). For the purposes of this report, the term "dioxins" is meant to refer to the set of 29 congeners in the polychlorinated dioxin/furan/biphenyl group that bind to the aryl hydrocarbon (Ah) receptor and possess toxic characteristics similar to those of *2,3,7,8*-tetrachlorodibenzo-*p*-dioxin (TCDD). These 29 congeners are listed in Table 1.

In this study and report, greatest emphasis is placed on the 17 PCDD and PCDF congeners with TCDD-like activity, since PCBs are not considered to be chemicals of concern at RMA, and because the current USEPA soil screening levels for dioxins (USEPA 1998) are based only upon these congeners. However, the 12 PCB congeners with TCDD-like activity were included in the study and analyses for reasons of a) completeness for background characterization, and b) to help resolve mass-balance comparisons with TCDD bioassays that were conducted for RMA tissue samples and which could be performed (if needed) on soil samples.

Table 1. List of Analytes and TEFs

Class	Target Analyte	TEF		
		Mammals	Birds	Fish
Dibenzo-p-dioxins (PCDDs)	2,3,7,8-TCDD	1	1	1
	1,2,3,7,8-PeCDD	1	1	1
	1,2,3,4,7,8-HxCDD	0.1	0.05	0.5
	1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
	1,2,3,7,8,9-HxCDD	0.1	0.1	0.01
	1,2,3,4,6,7,8-HpCDD	0.01	< 0.001	0.001
	OCDD	0.0001	0.0001	<0.0001
Dibenzofurans (PCDFs)	2,3,7,8-TCDF	0.1	1	0.05
	1,2,3,7,8-PeCDF	0.05	0.1	0.05
	2,3,4,7,8-PeCDF	0.5	1	0.5
	1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
	2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
	1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
	OCDF	0.0001	0.0001	<0.0001
PCBs	3,3',4,4'-TCB (77)	0.0001	0.1	0.0005
	3,4,4',5-TCB (81)	0.0001	0.05	0.0001
	3,3',4,4'-5-PeCB (126)	0.1	0.1	0.005
	3,3',4,4',5,5'-HxCB (169)	0.01	0.001	0.00005
	2,3,3',4,4'-PeCB (105)	0.0001	0.0001	< 0.000005
	2,3,4,4',5-PeCB (114)	0.0005	0.0001	< 0.000005
	2,3',4,4',5-PeCB (118)	0.0001	0.00001	< 0.000005
	2',3,4,4',5-PeCB (123)	0.0001	0.00001	< 0.000005
	2,3,3',4,4',5-HxCB (156)	0.0005	0.0001	< 0.000005
	2,3,3',4,4',5'-HxCB (157)	0.0005	0.0001	< 0.000005
	2,3',4,4',5,5'-HxCB (167)	0.00001	0.00001	< 0.000005
	2,3,3',4,4',5,5'-HpCB (189)	0.0001	0.00001	< 0.000005

TEF = Toxicity Equivalency Factor

TEF values are consensus estimates recommended by WHO (Van den Berg et al. 1998)

Relative Toxicity of Dioxin Congeners

Dioxins are of potential health concern because they may pose an increased risk of cancer and other non-cancer adverse health effects at extremely low levels of exposure. However, not all dioxin congeners are equally toxic. The relative toxicologic potency of a congener, compared to that of the most toxic form (*2,3,7,8*-TCDD), is expressed in terms of the Toxicity Equivalency Factor (TEF). Table 1 lists the current consensus TEF values for mammals (including humans), birds, and fish. These TEF values were developed by a panel of experts assembled by the World Health Organization (WHO) (Van den Berg et al. 1998), and have been adopted for use by the USEPA (USEPA 2000). It should be noted that TEFs are often based on limited data, and so they are recommended for use as only approximations of the relative toxicity of each congener, rounded to the nearest half order of magnitude.

Calculation of TCDD-Equivalents (TEQ) in Soil

The aggregate toxicity of a mixture of different dioxins in an exposure medium (soil, food web items, water, etc.) is a complex function of the following variables:

a) the concentration of each congener in the medium
b) the chronic average daily intake of the medium
c) the absorption of each congener from that medium
d) the toxicokinetics (distribution, metabolism, and elimination) of the congeners
e) the relative biological potency of the congeners

Thus, calculation of health risk from exposure to soil that contains a mixture of congeners must take all of these variables into account. However, for purposes of screening-level evaluations of dioxin concentrations in soil samples, it is usually most convenient to calculate the concentration of TCDD-Equivalents (TEQ) present in the soil as the TEF-weighted sum of each of the 29 dioxin-like congeners (17 dioxins and furans, plus 12 PCBs), as follows:

$$\text{TEQ (total)} = \sum_{i=1}^{29} (C_i \cdot TEF_i)$$

In cases where interest is focused on the contribution of PCDDs and PCDFs only (i.e., PCBs not included), the value is calculated as:

$$TEQ\ (D / F) = \sum_{i=1}^{17} (C_i \cdot TEF_i)$$

It is important to understand that this application of TEFs to the calculation of soil TEQ values is appropriate only for screening level purposes. This is because TEFs are derived from, and thus should only be applied to, biological endpoints (e.g., embryotoxicity). The soil TEQ approach does not account for the potential influences of differential absorption, metabolism, distribution, and excretion of different congeners from soil, and risk assessors should account for these uncertainties in the interpretation of the soil TEQ values.

1.3 Human Health Based Reference Values for Dioxins in Soil

The USEPA has currently established a default concentration value of 1,000 parts per trillion (ppt) TEQ in surface soil as a concentration that is not of cancer or non-cancer concern for lifetime exposure of residents (USEPA 1998a), even when no other site-specific data are known. For commercial and industrial land uses, USEPA guidelines identify 5,000 to 20,000 ppt TEQ as the concentration of concern in soil. These soil screening concentrations are based only upon the 17 TCDD-like PCDDs and PCDFs, calculated using the TEFs for mammals recently recommended by the WHO (Van den Berg et al. 1998).

The Agency for Toxic Substances and Disease Registry (ATSDR) has also established an interim policy guideline for human (residential) exposure to dioxin and dioxin-like compounds in soil (De Rosa et al. 1997). ATSDR identifies a concentration of 50 ppt TEQ in soil as a "screening level," below which no further investigation or characterization will usually be required. ATSDR identifies a concentration of 1,000 ppt TEQ as an "action level," indicating that public health actions such as surveillance, research, health studies, community education, or exposure investigations should be considered. Concentrations between 50 ppt and 1000 ppt TEQ are identified as "evaluation levels," indicating that further investigation of site-specific factors regarding the extent and possible public health implications of the exposure may be warranted.

The USEPA is in the process of completing a comprehensive reassessment of dioxin toxicity, and has tentatively concluded that the carcinogenic and non-carcinogenic potency of dioxins may be somewhat greater than previously believed (USEPA 2000). However, until a complete peer review and cross-program policy assessment of the impacts of this report can be

performed, USEPA recommends that the 1,000 ppt TEQ concentration in surface soil continue to be used as a soil screening level for residential land uses (USEPA 1998a), and that 5,000 ppt TEQ be used as a frame of reference for assessing exposure of commercial workers.

2.0 METHODS

A detailed description of the rationale, methods, and Standard Operating Procedures (SOPs) used in this study is provided in the Project Plan for the study (USEPA 1999). A summary of key elements of the study design and of the methods employed is presented below.

2.1 Sampling Locations

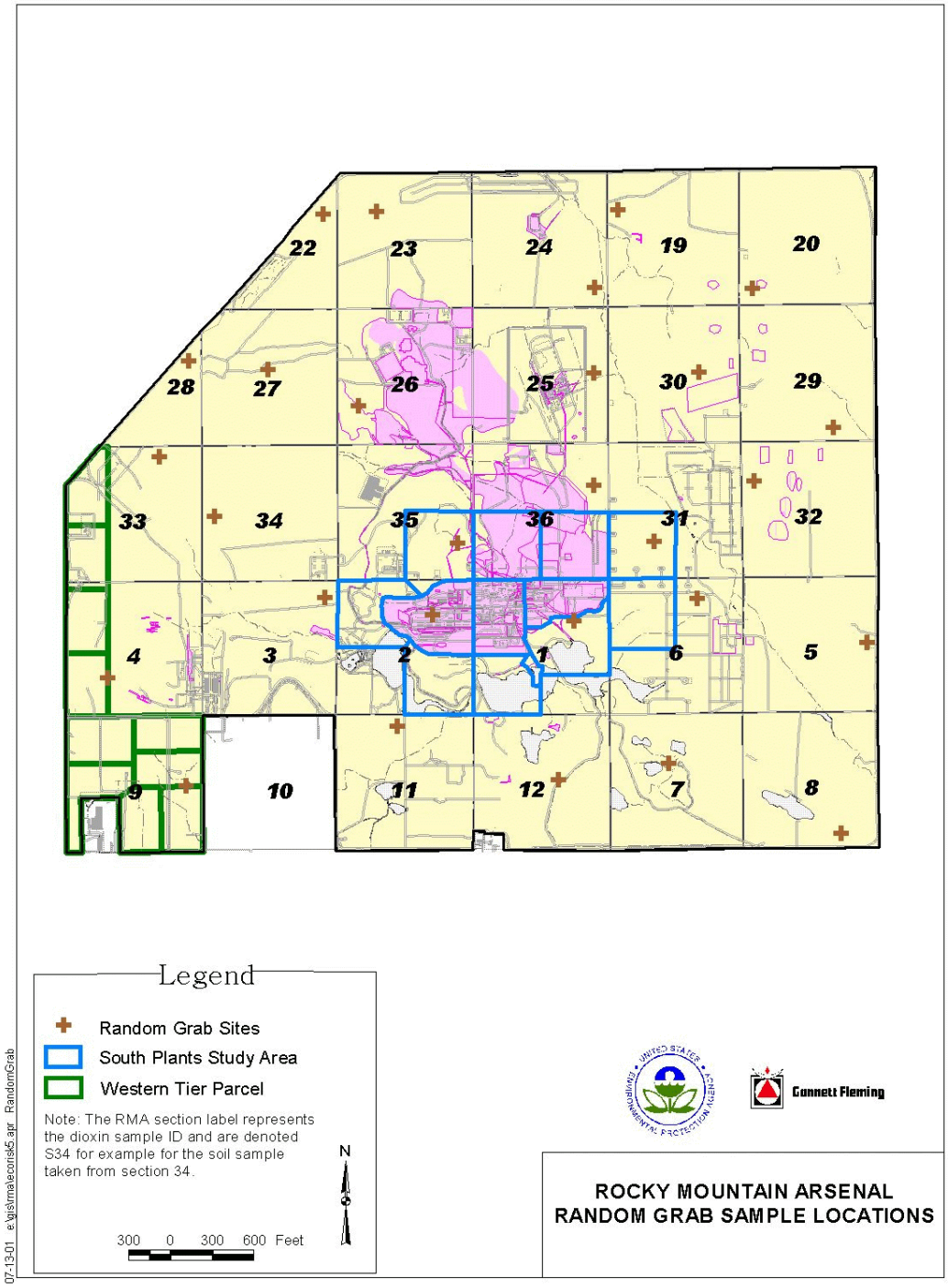
As noted above, RMA is an area of approximately 27 square miles. As shown in Figure 1, this area is divided into 28 Sections. One grab sample was collected from each section at a randomly selected location. These sampling locations are indicated by red "x's" in Figure 1. Detailed information on each of the sampling locations is provided in Appendix C.

2.2 Sample Collection and Storage

Because dioxins nearly always bind tightly to soil, it is expected that any dioxin contamination in soil attributable to atmospheric fallout, application of pesticides, or surface disposal of dioxin-contaminated material will be restricted mainly to the surface. Thus, surface soil is the exposure medium of chief concern for both human and ecological receptors. Therefore, all soil samples collected for this study were grab samples collected at 0-2 inches in depth.

Samples were collected using clean techniques that included use of disposable stainless steel trowels (one per sampling location) and plastic gloves. A ruler was used to ensure that the actual depth to which soil was collected was within ½ inch of the target (i.e., a bottom depth of no less than 1.5 inches and no greater than 2.5 inches). Loose debris and most gravel or pebbles were removed from the soil sampling site. The surface soil was placed directly into a clean 16-ounce amber glass jar, filled to capacity (about 500 grams of soil), sealed with a teflon-lined lid, and stored in these bottles at room temperature in the dark until shipped in sealed plastic coolers

Figure 1. Random Sampling Locations at the Rocky Mountain Arsenal



with frozen ice-packs and water temperature tubes that helped ensure no excess heating occurred during transportation to the processing laboratory.

2.3 Sample Preparation

All soil samples collected in the field were submitted under chain-of-custody to Columbia Analytical Services (CAS) for sample preparation. Each sample was air-dried and weighed, followed by coarse-sieving through a #10 (2 millimeter) stainless steel screen. The fraction passing the coarse screen is referred to as the "bulk" fraction. A portion of the bulk composite sample was placed in a clean amber glass jar and stored for possible future use, while the remainder of the bulk sample was further sieved through a 60-mesh (250 micrometer) stainless steel screen in order to isolate soil particles less than 250 micrometer in diameter. This is referred to as the "fine" fraction. Each fine-sieved soil sample was thoroughly mixed and placed into four new amber sample bottles, with each bottle containing about 26 grams of the fine-sieved soil. These four aliquots of fine-sieved soil were intended to be as identical as possible, for use in reanalysis (if needed) and for establishing intra-laboratory and inter-laboratory reproducibility (precision) for quality control purposes. All processed soil samples were sent under chain of custody to the USEPA Regional Laboratory in Golden, CO, for storage and for organization of samples for later shipments to the analytical laboratory in Kansas City, MO.

The "fine" fraction was isolated for chemical analysis because it is believed that fine soil particles can electrostatically adhere to skin and thus are more likely be ingested by hand to mouth contact than coarse particles. Hence it is concluded that the fine soil fraction is the most relevant media for use in evaluating human health risk. The bulk soil samples were retained for purposes of evaluating the potential enrichment of TEQ concentrations in the fine-sieved fraction due to small soil particles having greater surface to mass ratios than their bulk soil counterparts. It should be noted that most historic soil sampling studies for dioxins have only evaluated bulk soils, and so consideration needs to be given when comparing historic bulk dioxin results and the results for dioxin TEQs in this study's fine soil samples. If enrichment is present, it would cause the fine soil fractions to have greater concentrations of TEQs than their corresponding bulk counterparts, and bulk soil results would tend to underestimate exposure.

2.4 Sample Analysis

Following sample preparation as described above, samples were submitted by USEPA Region 8 under chain of custody to Midwest Research Institute (MRI) for congener-specific analysis of PCDDs, PCDFs, and PCBs. This type of analysis requires sophisticated extraction and clean-up procedures to accurately measure all of the various forms of PCDDs, PCDFs, and PCBs, as detailed in Standard Operating Procedure 11 of the Project Plan USEPA (1999). In brief, the congeners are determined using an isotope dilution method via high resolution gas chromatography/mass spectrometry (HRGC/HRMS). Samples are fortified with known quantities of ^{13}C-labeled PCDD/PCDF/PCB isomers and extracted with organic solvents, using two columns so that all 12 PCBs can be retained for analysis. Before cleanup of the extracts, the analytes are exchanged into hexane and fortified with ^{37}Cl-labeled *2,3,7,8*-tetrachlorodibenzo-*p*-dioxin. Finally, the extracts are sequentially partitioned against concentrated acid and base solutions.

The Method Detection Limit (MDL) for this study-specific analytical method was defined as an analyte signal that was 2.5 times the average background signal ("noise"). An estimate of the average signal noise is available for each analyte in each sample, so the MDL varies from sample to sample and from analyte to analyte. The Method Quantitation Limit (MQL) is based partly on the lowest calibration standard used, and was defined as a signal that was 10-times the average signal noise. Because the noise level varied from sample to sample and analyte to analyte, MDLs and MQLs also varied from sample to sample and from congener to congener. Most PCDD/PCDF congeners had MQL values between 0.03 and 1.3 parts per trillion (ppt), and most PCB congeners had MQLs between 0.2 and 5.4 ppt.

2.5 Quality Assurance

A number of steps were taken to obtain data that would allow an assessment of the quality and reliability of the data collected, so that assessments of the scientific usability of the data could be made and defended. The analytical laboratory routinely processed and analyzed "lots" (batches) of 20 samples at a time. Of these 20 samples, two were used for laboratory control samples (LCS) and blanks. Therefore, 18 samples were usually available for USEPA to submit to MRI as a batch. In general, these 18 samples were comprised of 14 field samples plus four Quality Control (QC) samples, as described below.

Performance Evaluation Samples

Performance Evaluation (PE) samples are samples of soil that contain known quantities of analyte and that are submitted blind to the analytical laboratory. In this study, three different PE samples were used. These were obtained from USEPA's Quality Assurance Technical Support (QATS) laboratory. Nominal values (ppt as TEQ in bulk soil, based on the 17 PCDD/PCDF congeners only) are listed below:

Table 2. Nominal TEQ(D/F) Concentrations in PE Samples

PE Sample (Bulk Soil)	**Nominal TEQ(D/F) (ppt)**
Native western soil (estimated value)	< 2
Low standard (certified value)	35
Medium standard (certified value)	59

One aliquot of each these three PE samples from QATS was submitted to the laboratory along with each batch of field samples.

Field Splits and Duplicates

A field duplicate is a second sample of soil collected simultaneously with the first sample. In this case, field duplicates were collected by alternating scoops of soil into two bottles with separate and random sample identification numbers. A field split is a sample that is generated by dividing a single field sample into two parts. As described above, in this study every field sample was dried and sieved by CAS, and this fine material was divided into four essentially identical aliquots of 26 grams each. EPA Region 8 selected random samples to submit as split samples, and a second bottle of these samples was assigned a new random sample identification number and submitted in random order for analysis by MRI. Analysis of these types of samples provided data on the variability within and between related samples. One sample of this type (either field split or field duplicate) was submitted to the laboratory (blind) with each set of 14 field samples.

Laboratory Quality Control Samples

Internal laboratory quality control samples are samples prepared and run by the laboratory in a non-blind fashion to monitor the performance of the analytical method. Laboratory QC samples included Method Blanks (analyte-free soil), Laboratory Control Samples (similar to PE samples, but the identity and true concentration are known to the laboratory), and optionally Method Duplicates (investigative samples that are split prior to sample preparation at the analytical laboratory). As noted above, two samples in each batch were used by the laboratory for laboratory QC samples.

2.6 Data Validation/Verification

Validation of analytical results was conducted according to SOP 803 (revision 1) of the Project Plan (USEPA 1999). This validation method was tailored to match the site-specific method used to analyze the 29 dioxin-like congeners in soils. An independent contract chemist team, with expertise in validation of PCDD, PCDF, and PCB analytical results, conducted the analytical reviews. Full validation was performed for all samples.

Major analytical factors and QA/QC performance were reviewed against defined Precision, Accuracy, Representativeness, Comparability, and Completeness (PARCC) criteria to ensure that results were reliable and usable for the objective identified in the Project Plan . Narratives were produced for each analytical lot to describe the results of the data validation for that lot. Each data value (i.e., each concentration value) was assigned a data usability flag, if needed, using the data quality flag codes presented in Table 3. In accordance with USEPA data usability guidelines (USEPA 1992), these flags were used for producing two alternative data sets:

1) a semi-quantitative set of results in which congeners that yielded signals below the sample-specific detection limit for that congener (signal/noise ratio less than 2.5) were evaluated by assuming a concentration value equal to ½ the detection limit for that congener, and other flagged data were adjusted according to the rules shown in Table 3. This is referred to in this report as the "**Full**" data set.

2) a quantitative set of results based only on those congeners that have no disqualifying flags (D, NJ, R and LT), or have adjusted quantitative values as described in Table 3. This is referred to in this report as the "**Quant**" data set.

Table 3. Definition, Application, and Uses of Data Flags

Validation Flags	**Meaning of Flags** for Dioxin Analyses in Soils and Tissues by the MRI Lab	Data Usability (a)	
		Full data set used (*semi-quantitative*)	**Quantitative** (qualified sub-set used)
E	**E**stimated Maximum Potential Concentration; the relative ion abundance ratios did not meet the acceptance limits.	use value	use ½ value
D	EMPC is caused by polychlorinated **D**iphenyl ether interference.	use ½ value	don't use
B	Analyte was detected in associated Method **B**lank, sample concentration <5x MB concentration.	use value	use ½ value
C	Concentration is above upper **C**alibration Standard; result is an estimate, flagged C by lab and J added by validator.	use value	use value
I	Recovery of 13C-labeled **I**sotopic analyte outside of criteria	use value	use value
J	Estimated: e.g., isotopic standard is outside CCAL range, native analyte recovery in LCS is outside criteria, etc.	use value	use ½ value
NJ	Presumptive evidence for the presence of an analyte with an estimated value; if used for 2378-TCDF, see "U" below.	use ½ value	don't use
S	Peak is **S**aturated; result, if calculated, is flagged by the validator as an estimate - "J".	use value	use value
U	**U**nconfirmed: column is not specific for 2,3,7,8-TCDF; confirmation not requested. Validator now uses "NJ" flag.	use value	use ½ value
R	**R**ejected: result is invalid and not usable.	use ½ MDL	don't use
***use of MRI Laboratory's reported "LT" (less than) values* <MQL (10 x Signal:Noise)**			
LT *applied **first** to data, then apply flags!*	"LT" is not a true "flag", but if a LT result is a "**detect**" **above the MDL** (2.5 x Signal:Noise = lab EDL), then	use value	use ½ value
	"LT" is not a true "flag", but if a LT result is a "**non-detect**" **below the MDL** (2.5 x Signal:Noise = lab EDL), then	use ½ EDL	don't use

(a) In accord with concepts in the 1992 EPA Data Usability for Risk Assessment in Superfund guidance (USEPA 1992), data quality flags are used to produce two data-sets: 1) a "**Full**" set of semi-quantitative results with an **actual** or a **proxy** value for each of the measured congeners; and 2) a more "Quantitative" but limited set of results that has more certain identification and more accurate quantities of congeners which have **no disqualifying flags** (D, NJ, R or LT), but can use **limited proxies** (E, B, J or U). This distinction is made to better understand and limit artifactual impacts of the *less certain **estimated** values* on TEQs,analyzing the degree of this sensitivity to trace-level "noise" by comparing TEQs from these two data sets. In addition, congener profile pattern analysis should only use the analytes that are quantifiable (above the MQL).

These two datasets were prepared to help evaluate the magnitude of effects of estimated values from the Full dataset on TEQs, and to show how the quantitative subset of results can be properly derived to statistically evaluate the profiles of congeners in soils. In general, the Full TEQ(D/F) results are considered to be the most relevant in evaluating potential health risks from dioxins.

3.0 RESULTS

Detailed analytical results for each field sample are presented in Appendix A1, and detailed results for each QA sample run as part of this study are presented in Appendix A2. Graphical representations are presented in Appendix B. The results are summarized below.

3.1 Data Validation Results

Full validation of the data found the analytical results to be usable, as qualified with the appropriate data quality flags (see Appendix A).

3.2 TEQ Values in Field Samples

Table 4 presents the results (expressed as ppt of TEQ) for each of the 28 grab samples collected during the study. The spatial pattern for Full TEQ(D/F) is presented in the map in Figure 2.

As seen, most samples (25 out of 28) had full TEQ values that were less than 3 ppt. Full TEQ(D/F) values were slightly elevated (compared to the rest of the samples) in Section 1 (25 ppt), Section 2 (7 ppt), and Section 35 (4 ppt), all of which are located in the South Plants area of RMA. As discussed in USEPA (2001b), other samples collected in this area support the conclusion that dioxin levels are slightly elevated compared to the rest of RMA in the South Plants area, but that contaminant levels tend to fall off rapidly as a function of distance from this historic source area.

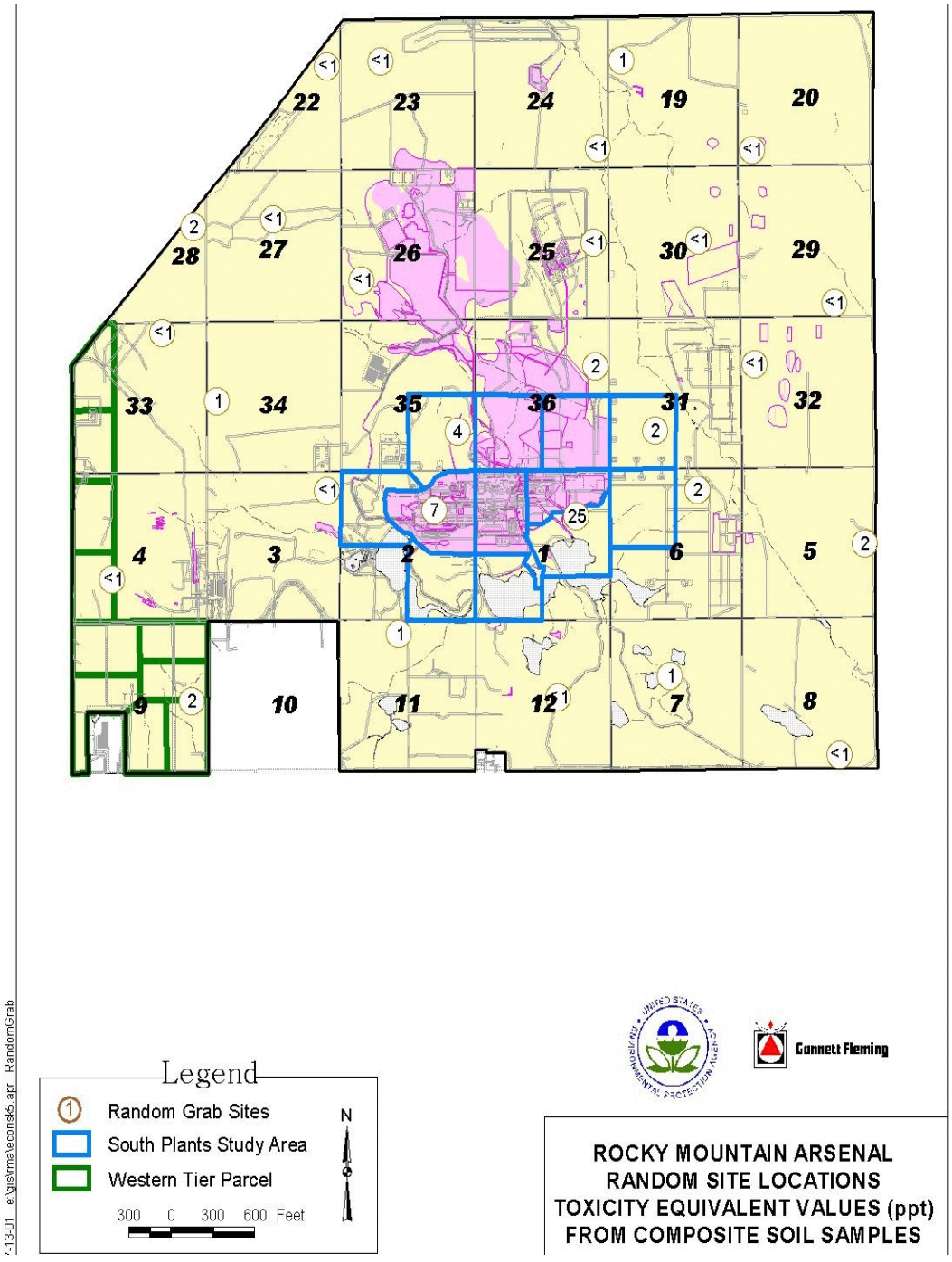
Comparison of the values for Full and Quant TEQ in Table 4 reveal that in most cases the two values are similar, especially for the samples with elevated levels, with an average difference of about 0.2-0.3 ppt. This indicates that congeners at or below the quantitation limit do not contribute strongly to the Full TEQ value.

Table 4. TEQ Values for RMA Random Grab Soil Samples

Section	Dioxin/Furan Only		PCBs Only		Total	
	Full	Quant	Full	Quant	Full	Quant
S1	25.3	24.6	0.8	0.5	26.1	25.1
S2	7.2	7.0	1.2	1.1	8.3	8.1
S3	0.7	0.6	0.3	0.2	1.0	0.8
S4	0.6	0.4	0.5	0.3	1.1	0.7
S5	1.8	1.5	0.2	0.2	2.0	1.7
S6	1.6	1.3	0.2	0.2	1.9	1.5
S7	1.0	0.9	0.4	0.4	1.4	1.3
S8	0.3	0.2	0.1	0.1	0.4	0.2
S9	1.6	1.4	1.2	0.7	2.8	2.0
S11	1.0	0.8	0.6	0.6	1.6	1.4
S12	0.7	0.4	0.3	0.3	1.1	0.7
S19	1.3	1.2	0.8	0.8	2.0	2.0
S20	0.7	0.4	0.2	0.2	0.9	0.6
S22	0.7	0.5	0.3	0.3	1.1	0.8
S23	0.3	0.2	0.1	0.1	0.5	0.3
S24	0.3	0.2	0.2	0.2	0.5	0.3
S25	0.1	0.0	0.0	0.0	0.2	0.0
S26	0.8	0.7	0.3	0.1	1.1	0.8
S27	0.2	0.2	0.2	0.1	0.4	0.3
S28	1.5	1.3	1.2	0.7	2.7	1.9
S29	0.3	0.2	0.1	0.1	0.4	0.3
S30	0.5	0.2	0.1	0.1	0.7	0.4
S31	2.0	1.7	0.4	0.4	2.3	2.0
S32	0.8	0.5	0.2	0.2	1.0	0.8
S33	0.8	0.6	0.8	0.4	1.6	1.0
S34	0.9	0.9	0.7	0.7	1.7	1.6
S35	3.5	3.2	1.5	0.8	5.1	4.0
S36	1.5	1.3	0.5	0.4	2.0	1.7

All TEQ values are expressed in units of ppt

Figure 2. Full TEQ(D/F) for Random Grab Samples at RMA



3.3 Comparison to Risk-Based Guidelines

In accordance with the Project Plan developed before implementation of this study, the potential health risk to on-site workers from future exposures to dioxins in RMA soils was evaluated by comparing the TEQ concentration value in each grab sample with the USEPA default health-based reference range of 5,000-20,000 ppt identified by USEPA as the potential level of concern for workers (EBASCO 1994). Inspection of Figure 2 and Table 4 reveals that all of the samples collected in this study, including the samples from near the South Plants area of the site (the region with the greatest impact from historic releases), the Full TEQ for PCDDs and PCDFs are all far below the level of potential health concern to workers:

USEPA Health Criterion for Workers:	5000 ppt
Maximum RMA Random Grab sample:	25 ppt
Mean RMA Random Grab sample:	2.1 ppt

It should also be noted that the areas of RMA with the highest dioxin levels (including South Plants) are currently scheduled for soil remediation due to the presence of organochlorine pesticide contamination. Once this remediation is complete, it is expected that dioxin levels across RMA will be approximately the same as for any other open space area in the Denver Front Range area.

3.4 Contribution of PCBs

As shown in Table 4 (center section), the concentration of PCBs (expressed as TEQ) in the random RMA soil samples is usually less than 1 ppt, with an average across all samples of 0.5 ppt. In these samples, PCBs contribute from 3% to 51% of the total, with an average across all 28 samples of about 30%.

3.5 Contribution of Congeners Below the Quantitation Limit

As noted above, in the calculation of the Full TEQ value for a sample, all congeners that were below the detection limit (signal/noise ratio < 2.5) were evaluated by assuming a concentration value equal to ½ the detection limit. This is the approach is that is normally used to evaluate chemicals of concern at Superfund sites (USEPA 1989). In order to evaluate the relative contribution of congeners that were either not detected, or else were present at such low

concentrations that their true concentration could only be estimated, a second calculation of "Quant" TEQ was performed, which included only those congeners that were detected above the quantitation limit (signal/noise > 10). Other occasional adjustments to reported concentrations of congeners were made when certain qualifier flags were assigned to the result, based on the criteria shown in Table 3.

For the 28 random grab samples from RMA, the average ratio of Full TEQ(D/F) to Quant TEQ(D/F) was 1.26. For TEQ(Total), the ratio of Full TEQ to Quant TEQ was 1.25. This indicates that congeners bellow the quantitation limit contribute an average of about 25-26% to the TEQ values at random soil sampling locations at RMA.

3.6 Comparison of Bulk to Fine Samples

As noted earlier, all soil samples were prepared by sieving to isolate the “fine” fraction of particles less than 250 micrometers in diameter, since it is believed that this size fraction is likely to be of greater relevance to human exposure than the bulk fraction. However, since most other studies of dioxin concentrations in soil have used un-sieved soil, throughout the project some bulk soil samples were also analyzed to allow a comparison of concentration values in the bulk and fine fractions. In this particular study, only one such bulk sample (from Section 2) was analyzed. In this sample, the ratio of Full TEQ(D/F) in the fine fraction divided by that in the bulk sample was 1.24, and the ratio for Full TEQ(Total) was 1.22. Because this ratio is based on only one sample, no firm conclusions can be drawn. However, if a similar enrichment in the fine fraction were to be general, then evaluations of dioxin TEQs that are based only on analyses of bulk samples may tend to underestimate human health risk.

3.7 Quality Control Samples

Quality control samples that were analyzed as part of this study indicate that the data are reliable and accurate, as described below.

Method Blanks

Four method blanks were included with the samples for this study. The values for Full TEQ (total) ranged from 0.1 to 0.6 ppt (mean = 0.3 ppt). This indicates that there is no significant source of PCDD, PCDF or PCB contamination within the analytical laboratory.

Splits and Duplicates

TEQ(D/F) values for duplicate and split pairs are as follows:

Table 5. Evaluation of Precision in Sample Pairs

Sample	Full TEQ(D/F) (ppt)	Quant TEQ(D/F) (ppt)
S-1 S-1 Split	25.3 6.9	24.6 6.7
S-5 S-5 Split	1.8 1.1	1.5 0.2
S-23 S-23 Dup	0.3 0.4	0.2 0.3
S-35 S-35 Split	3.5 3.1	3.2 2.7

As seen, except for the first pair (S-1), there is good agreement between splits and duplicate pairs, with an average difference of less than 1 ppt, which is well within the acceptability criterion of 1 MQL (about 5 ppt TEQ) that was established by the Project Plan (USEPA 1999) for low-concentration samples. The basis for the discrepancy between the original and split result for sample S-1 is not known, but is considered to be atypical.

Performance Evaluation Samples

Analytical results for the soil standards (PE samples) obtained from the USEPA QATS laboratory are summarized below.

Table 6. Evaluation of Accuracy Using Certified PE Samples

PE Sample	Certified Conc. (ppt)	N	Measured TEQ(D/F) (ppt)	
			Full	Quant
Low Standard (bulk)	35	2	47.5 ± 3.2	47.3 ± 3.1
Medium Standard (bulk)	59	2	74.8 ± 1.9	73.5 ± 0.3

As seen, measured values for bulk PE samples are somewhat higher than but are still in reasonable accord with the expected (nominal) values.

Five samples of the "Clean Soil" PE sample provided by the QATS laboratory were also analyzed on an on-going basis throughout the study. This is the soil used by QATS contractors for spiking with TCDD-like congeners to produce the PE standard soils. This soil sample was estimated to contain less than 2 ppt TEQ in the bulk fraction, but this was not a certified value. The samples of Clean Soil analyzed in this study were sieved to isolate the fine fraction before analysis, so the expected value in the fine fraction is not known. However, analytical results were low (1.8 ± 0.8 ppt Full TEQ(D/F) and 1.6 ± 0.9 ppt Full TEQ(Total)), consistent with the estimated values in the bulk soil. Because these samples were submitted to CAS in parallel with field samples, these results establish that there is no significant source of contamination during the sample preparation or the sample analysis steps.

Laboratory Spikes

Four different laboratory spikes were analyzed in association with the field samples from this study. Spike concentrations were 20 ppt for TCDD and TCDF, 100 ppt for each of the penta-, hexa- and hepta-PCDDs and PCDFs, and 200 ppt for OCDD, OCDF, and each of the PCBs. Based on this spiking mixture, the nominal TEQ(D/F) is 250 ppt, and the nominal TEQ(Total) is 272.5 ppt. Average recovery of individual PCDD/PCDF congeners ranged from 73% to 112%, with an average across all samples of 93%. Average recovery of individual PCBs ranged from 105% to 128%, with an average across all samples of 111%. When expressed as Full TEQ, recovery was 91% to 102% (mean = 97%) for TEQ(D/F), and was 92% to 103% (mean = 98%) for TEQ(Total). This indicates that matrix interference is not likely to be of concern.

4.0 DISCUSSION

4.1 Comparison to Denver Front Range Area Background Levels

Dioxins can be formed and released to the environment from a variety of sources, especially incinerators that burn medical and municipal wastes (USEPA 1994). In addition, dioxins can be formed in low levels from the combustion of coal and wood, and dioxins are released from power plants, wood burning furnaces, forest fires, etc. (USEPA 1998). As a

consequence of these multiple and widespread sources, dioxins are believed to be present in low concentrations in nearly all samples of surface soil.

Limited data are available in the literature on the concentrations of PCDDs and PCDFs in "background" soil. A summary of these data are presented in USEPA (2001c). In general, mean values for rural and urban areas are mainly in the 1-6 ppt range, although some lower and some higher values are reported. However, there are a number of limitations to these data (USEPA 2001c), so in order to strengthen the database for site-specific decision making, the USEPA Region 8 has recently completed studies of dioxin levels in a range of typical soils from multiple locations and land uses across the Denver Front Range (USEPA 2001c). Appendix D contains maps that summarize the results of this study, and Figure 3 compares the distribution of Full TEQ(D/F) values observed at the random sampling locations within RMA with values observed at sampling locations around the greater Denver Front Range area (USEPA 2001c). As seen, the TEQ(D/F) values at RMA are similar to levels observed in open space and agricultural areas, and are lower than values observed in commercial, industrial and residential areas. Multiple pair-wise comparisons using the Mann-Whitney rank sum test indicate that there is no statistical difference between the on-post random samples and the Denver Front Range data sets for open space ($p = 0.853$) or agricultural lands ($p = 0.900$), while the on-post random samples are different (lower) than the off-post commercial, industrial and residential data sets ($p < 0.01$). This indicates that, except for areas in the immediate vicinity of the former manufacturing area at RMA, there has been no detectable release of dioxins to RMA soils from a site-specific source.

4.2 Congener Composition

The congener composition of a soil sample may provide useful information about the source of the dioxin contamination, and helps to reveal which specific congeners are contributing the majority of the risk.

Appendix A shows the relative (percent) contribution of each of the 29 congeners to the total TEQ in each of the soil samples in this study. The mean contribution of each congener (percent contribution within a sample averaged across all samples) to TEQ is summarized in Table 7. As seen, most of the Full TEQ(Total) is contributed by PCB-126, *2,3,4,7,8*-PeCDF, *1,2,3,7,8*-PeCDD, *1,2,3,4,7,8*-HxCDF, *1,2,3,6,7,8*-HxCDF, and *1,2,3,4,6,7,8*-HpCDD.

Figure 3. Comparison of RMA Random Samples to Denver Front Range Soils

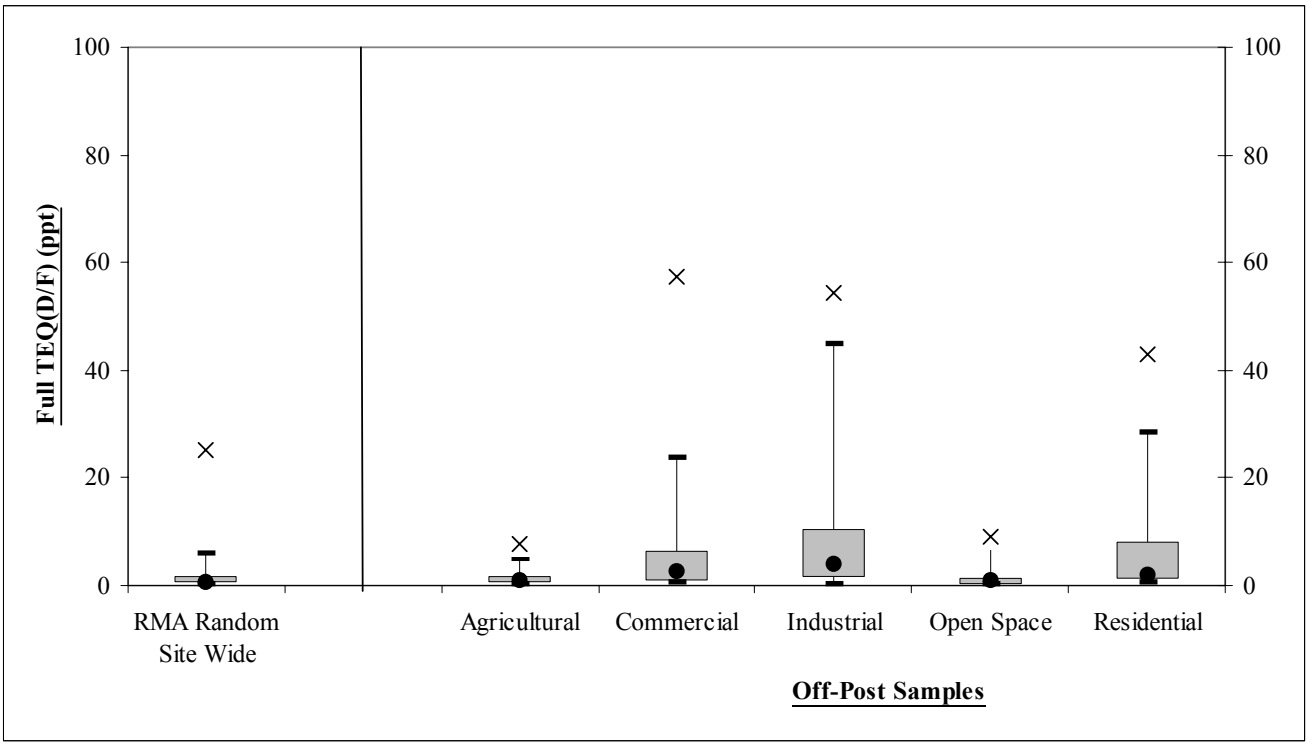


Table 7. Relative Contribution of Congeners to Total TEQ

Analyte	Mean Percent Contribution to the Total TEQ	
	Full	Quant
2,3,7,8-TCDF	1.3%	0.0%
2,3,7,8-TCDD	3.0%	2.6%
1,2,3,7,8-PeCDF	2.6%	2.9%
2,3,4,7,8-PeCDF	**9.5%**	**8.3%**
1,2,3,7,8-PeCDD	**9.4%**	4.7%
1,2,3,4,7,8-HxCDF	**8.4%**	**9.4%**
1,2,3,6,7,8-HxCDF	**5.3%**	**5.1%**
2,3,4,6,7,8-HxCDF	3.2%	3.0%
1,2,3,7,8,9-HxCDF	5.0%	4.4%
1,2,3,4,7,8-HxCDD	1.9%	1.5%
1,2,3,6,7,8-HxCDD	3.7%	3.9%
1,2,3,7,8,9-HxCDD	4.3%	**5.0%**
1,2,3,4,6,7,8-HpCDF	3.7%	4.7%
1,2,3,4,7,8,9-HpCDF	1.2%	1.3%
1,2,3,4,6,7,8-HpCDD	**7.2%**	**11.6%**
OCDF	0.3%	0.3%
OCDD	0.6%	0.9%
PCB-77	0.1%	0.1%
PCB-81	0.0%	0.0%
PCB-105	0.6%	0.7%
PCB-114	0.1%	0.1%
PCB-118	1.2%	1.3%
PCB-123	0.0%	0.0%
PCB-126	**25.8%**	**26.3%**
PCB-156	1.0%	1.3%
PCB-157	0.3%	0.3%
PCB-167	0.0%	0.0%
PCB-169	0.3%	0.3%
PCB-189	0.0%	0.0%
D/F Only	*70.5%*	*69.5%*
PCBs Only	*29.5%*	*30.5%*
Total	*100.0%*	*100.0%*

Cells greater than 5% have been shaded to highlight the main contributors

Appendix B1 presents a series of graphs showing the absolute chemical concentrations and TEQ contributions of each of the 29 congeners in each of the field soil samples collected during this study. Appendix B2 shows the aggregate concentrations and TEQ contributions for each of the five homologue classes of the 17 TCDD-like dioxins and furans. Appendix B3 shows the relationships between aggregate concentrations and TEQ contributions of dioxins compared to furans. Appendix B4 presents similar concentration graphs for QA samples. In all cases, greater emphasis is placed on the quantitative concentration data than the full concentration data for evaluation of congener concentration profiles.

Figure 4 summarizes the average quantitative congener concentration pattern in random RMA soils. The upper panel shows congeners in the PCDD/PCDF class, while the lower panel shows congeners in the PCB class. As seen in the upper panel, the primary congener in the dioxin/furan class is usually OCDD, although a very high level of OCDF along with several other hepta- and hexa-PCDDs and PCDFs were detected in Section 1. As seen in the lower panel, several PCBs are usually present, primarily 105, 118, 156, and 167.

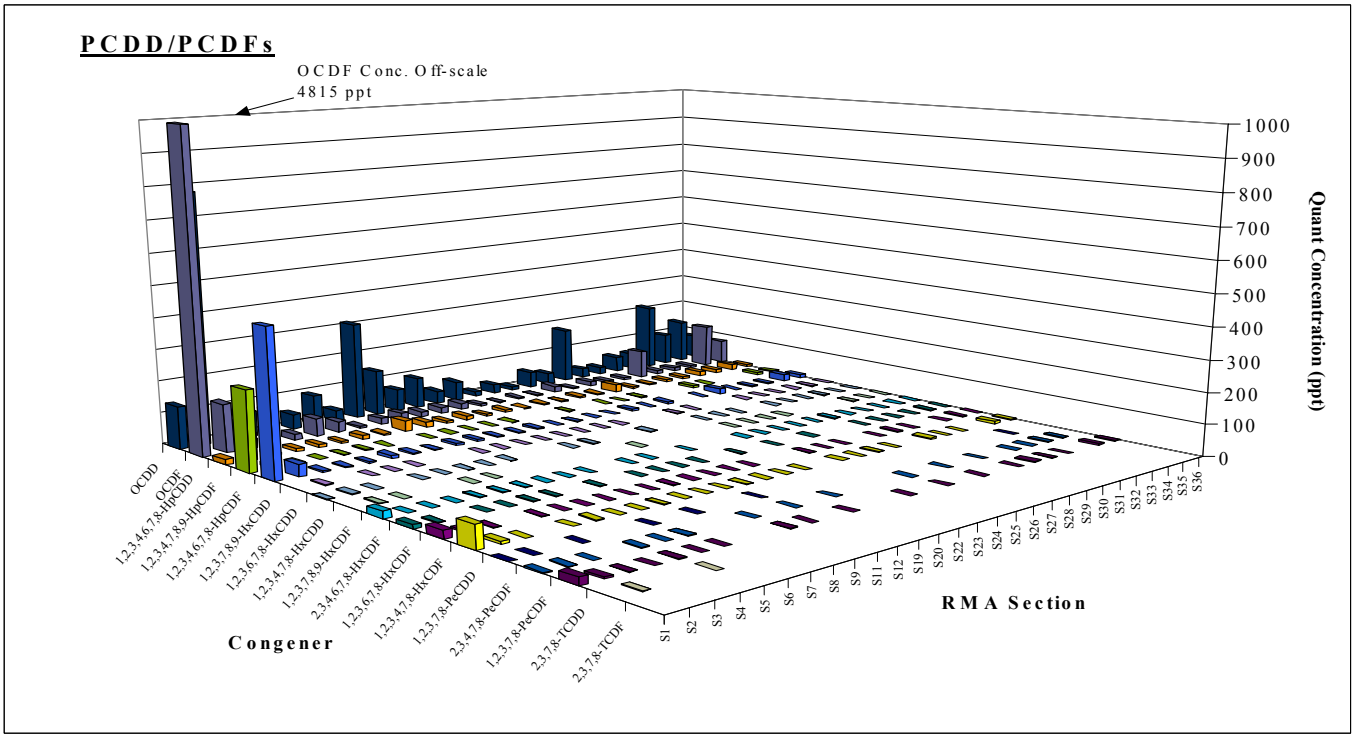
A more detailed and quantitative analysis of the congener concentration values in surface soil samples from the random areas of RMA along with results from other locations at RMA and from multiple locations and land uses around the Denver Front Range area will be presented in a subsequent report.

4.3 Dependence of TEQ on Soil Characteristics

Binding of dioxins to soil particles is a physical process that might be expected to depend on the total organic carbon (TOC) content of the soil, as well as the surface-area-to-mass ratio (i.e., the particle size distribution). Such a dependence of TEQ levels on soil characteristics has been noted by Rogowski et al. (1999), although these data are somewhat limited by use of TEQ values calculated from congener concentrations that were largely below the MDL.

Figure 5 (Panel A) summarizes the relationship between Full TEQ(D/F) and soil TOC. The data point for Section 1 was excluded from the analysis because the relatively elevated TEQ value in this Section is attributed to historic release from South Plant facilities. The data from Sections 2 and 35 were retained, since the impact of the South Plants area on these samples appears to be minimal. As seen, TOC levels ranged from about 0.5% to 2% in the soil samples, while Full TEQ(D/F) levels ranged from about 0.1 to 25.3 ppt. The slope of the best-fit linear

Figure 4. Average Congener Concentration Profile in Random RMA Soils



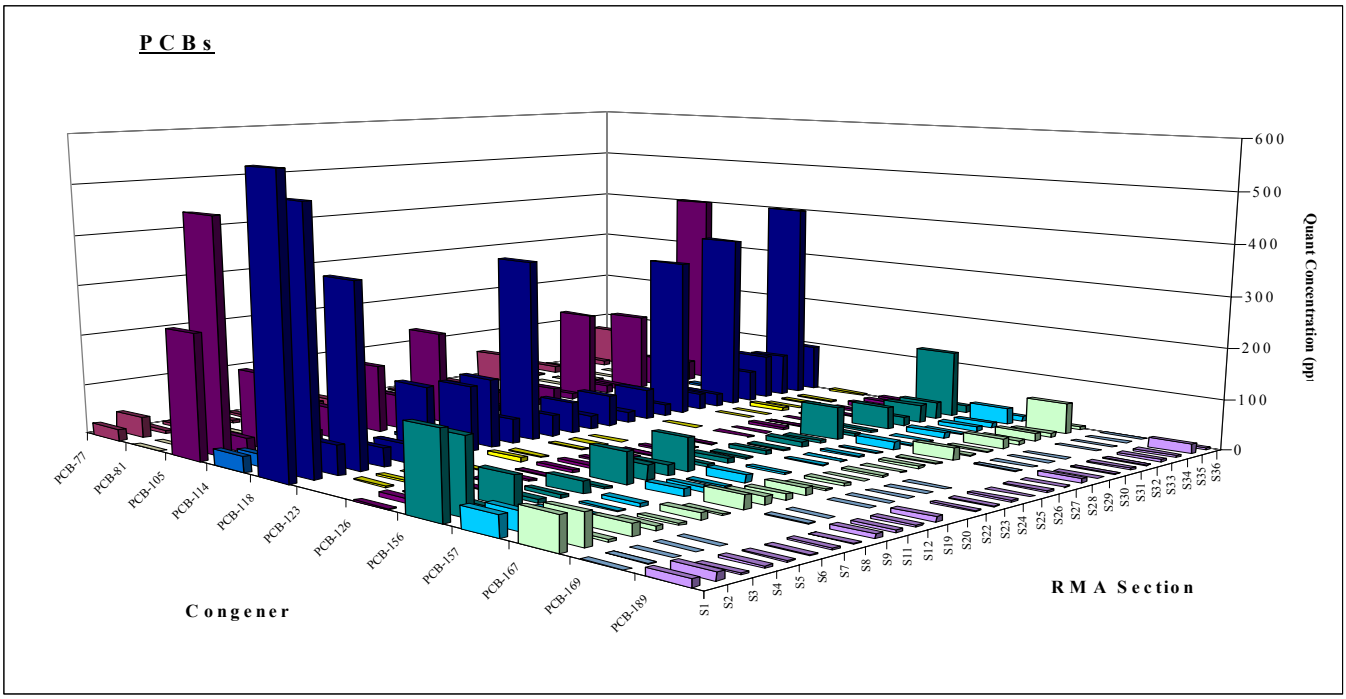
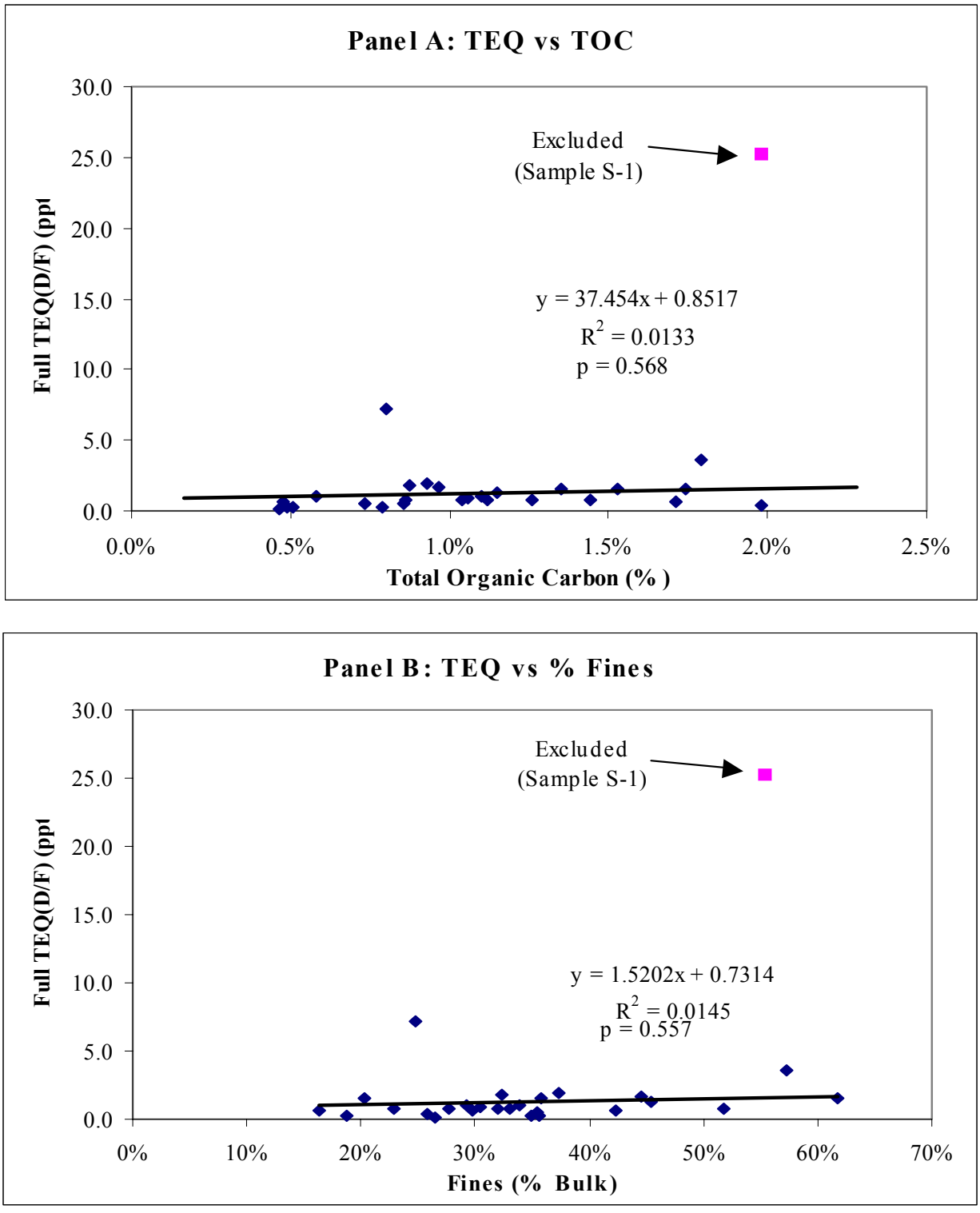


Figure 5. Dependence of TEQ on Soil Characteristics



regression line through the data is not statistically different from zero ($p > 0.5$), and the coefficient of determination is very low ($R^2 = 0.013$). This indicates that TOC is not a significant determinant of TEQ, at least in these soil samples.

Figure 5 (Panel B) shows the relation between Full TEQ(D/F) and the mass fraction of the raw field sample that passes a fine screen. As above, the slope of the best-fit linear regression line is not statistically different from zero ($p > 0.5$), and the coefficient of determination is very low ($R^2 = 0.0145$). This indicates that the fraction of fine particles in a soil is not a significant determinant of TEQ levels, at least in these soil samples.

5.0 SUMMARY AND CONCLUSIONS

The concentration of dioxins is low in most samples of soil collected from random locations at RMA, although small elevations are observable in some samples collected from areas close to the former chemical manufacturing operations (the South Plants area). The distribution of values across the site is not statistically different from values observed in open space and agricultural areas around the Denver front range area, and all of the on-site values are far below a level of health concern to on-site workers. It should also be noted that the South Plants area of RMA is scheduled for soil remediation due to the presence of organochlorine pesticide contamination, and once this remediation is complete, it is expected that dioxin levels throughout RMA will be approximately the same as for open space areas in the Denver Front Range area and will present no significant health risk to future Refuge workers, volunteers, or visitors.

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